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Citations:

DE	197 40 431 C1
DE	42 06 680 C1
DE	29 20 766 C2
US	58 49 170
US	46 71 968
US	42 65 943
US	42 09 331
EP	09 13 502 A1
EP	06 16 053 A1
EP	5 30 568 A2
WO	98 45 507 A1

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Method for the electrolytic metallization of dielectric surfaces

For the robust metallization of, in particular, larger electrically nonconducting surfaces, such as polymer surfaces, a method is proposed, which can be carried out simply without problems and safely without expensive monitoring methods.

It is therein ensured that the bath, unlike conventional electroless metallization baths, does not tend to self-decomposition. The method serves for the electrolytic deposition of a metal layer on surfaces of an electrically nonconducting substrate and comprises the following method steps: (a) activating the surfaces with an inert metal colloid, which is stabilized with compounds of a metal from main group IV of the Periodic System of Elements (PSE), (b) treating the activated surface with an alkaline solution comprising ions of a metal which is more inert than the metal from main group IV of the PSE, and at least one complex former for the metal ions, (c) treating the surfaces with a copper bath comprising at least one copper ion source, at least one reducing agent for the copper ions and at least one complex former for the copper ions, without application of an external current source, (d) depositing the metal layer electrolytically with a galvanization bath.

The invention relates to a method for the electrolytic deposition of a metal layer on surfaces of electrically nonconducting substrates, in particular on polymer surfaces. The invention further relates also to an application of the method for electrolytic metallization of polymer and copper surface regions on circuit boards, in particular of polymer resist layers on the circuit boards.

In the production of circuit boards metallic coatings are formed in order to set up electrical connections between the individual electric components and different wiring layers. The electrical connections are formed by the known subtractive, semi-additive, additive methods and other methods. The coatings on the surfaces of the circuit board material and on the walls of bores in the material are generated through electroless and electrolytic methods.

In the conventional electroless metallization methods the electrically nonconducting surfaces are most often activated with a palladium colloid, which is stabilized with tin compounds. Tin hydroxides are subsequently removed with suitable solutions (acceleration).

For the formation of an initial electrically conductive metal layer, an electroless copper deposition bath is conventionally employed. In this case, copper is deposited on the activated surfaces of electrically nonconducting surfaces from baths conventionally comprising formaldehyde as a reducing agent. However, the use of formaldehyde as a reducing agent in the electroless copper baths has been found to be highly disadvantageous. For one, formaldehyde is readily volatile and toxic, such that considerable safety problems are encountered when working with these baths. In addition, it was found that these baths react in a highly sensitive fashion to such parameters as, for example, fluctuations of bath component concentrations. For that reason alternatives have been proposed.

US 4,209,331 A for example describes an electroless copper deposition bath, which comprises copper ions, a complex former for the copper ions and, as a reducing agent, a hypophosphite ion source. Further, it is stated in the examples that the bath comprises 0.002 mol/L of nickel ions. The pH value of the bath is adjusted to values of 5 to 13. Treatment times of 5 to 20 minutes are listed. This bath is employed for the conventional electroless

metallization. According to the methods, an electrically nonconducting substrate is first activated with a conventional palladium/tin colloid and subsequently accelerated with a solution for the removal of tin hydroxides. With the described bath a copper layer can subsequently be formed electrolessly.

In US 4,265,943 A an electroless copper deposition bath is also placed under protection, with which even during a relatively long deposition period a constant deposition rate is said to be ensured. For this purpose, as to the bath according to US 4,209,331 A, to the bath are added nickel and, alternatively, cobalt ions, which are referred to as autocatalysis promoters. Treatment times in the range of 4 to 90 minutes are stated in the individual examples.

In US 4,671,968 A a method is placed under protection, in which an electroless formaldehyde-free copper deposition bath is utilized for the metallization of electrically nonconducting substrates. US 4,209,331 A is cited, according to which copper deposition baths described therein are said not to work autocatalytically. The patent therefore proposes to apply a current pulse for the initiation of the copper deposition for the generation of thicker copper layers. In contrast to US 4,265,943 A, this method is also said to permit, in addition, coating of even relatively large nonconducting surfaces of circuit boards over the entire surface. When using the bath specified in US 4,265,943 A, it is said not to be possible without further measures, for example, to continue the copper deposition again after interrupting the coating. Treatment time examples in the range of 15 to 30 minutes are given.

In the trade article “An Ecofriendly Electroless Copper Plating Process”, L.G. Bhatgadde and D. Joseph in “*Transactions of the Metal Finisher Association of India*, Vol. 6 (1997), pp. 55 to 60, electroless copper deposition baths are proposed for the conventional electroless copper deposition, in which sodium hypophosphite is utilized as a reducing agent. In addition to copper sulfate and sodium hypophosphite, one of the baths comprises cobalt sulfate and trisodium citrate as complex formers. The pH value is 12, the treatment time 30 minutes.

However, the use of the electroless copper deposition baths with hypophosphites as reducing agents has not become widely accepted. Therefore, so-called direct galvanization

methods, which suffice without process steps for the electroless metallization, have been used for the last few years. In these methods the metal layers are exclusively applied electrolytically.

Known is the direct metallization of bore hole walls in electric circuit boards with an organic polymer stabilized palladium colloid. Such a method is described, for example, in DE 42 06 680 C1. This method is characterized by the following method steps: (a) conditioning of the electrically nonconducting bore hole walls with a chelate former and/or a cationic surface-active substance, (b) treatment with a colloidal acidic solution of an inert metal stabilized by an organic polymer, (c) treatment with a solution comprising sulfinic acid, sulfites, thiosulfates, dithionites, dithionates or tetrathionates or their mixtures, (d) galvanic (electrolytic) metallization. This method permits deposition of a metal layer electrolytically on the nonconducting bore hole walls without the walls previously needing to be electrolessly metallized.

The method is suitable for the direct electrolytic metallization of the electrically nonconducting surface regions of the bore hole walls. Due to the lacking electrical conductivity of the conducting layer obtained with the palladium activation and subsequent posttreatment with sulfur compounds, however, a direct electrolytic metallization of circuit boards over the entire surface, which lack any copper lamination, is not possible. Such a metallization is applied, for example, in the so-called SBU method (Sequential Build-Up) for the generation of conductor structures on the outside of circuit carriers, in which an overall metallization having adhesive strength of the circuit board outsides must be achieved. If the method of DE 42 06 680 C1 is applied for such a method, the electrolytic metallization must therefore proceed at an extremely low current density, wherein, however, only a metal layer with highly nonuniform thickness can be deposited. In this case, a further problem is presented by the additional requirement that a metal layer having adhesive strength must be achieved on the outer surfaces of the circuit board.

Another direct galvanization method is disclosed in EP 0 530 568 A2. In this method a nonconducting substrate is first activated in the conventional manner after customary pretreatment steps with an inert metal colloid stabilized with tin compounds and subsequently

electrolytically metallized in a copperplating bath, which, in addition to a copper salt and a complexing means for copper ions, contains a reducing agent intended to activate the formed palladium nuclei. The copperplating solution has a pH value of approximately 6 to 7.5; the temperature of the solution is in the range of approximately 15 to 50°C. As reducing agents are proposed dimethylaminoborane, hydrazine and hypophosphites. Complex formers listed are for example also citric acid and citrates.

Disadvantages entailed in this method are that uniform coating of large areas is not possible, due to the extremely low electrical conductivity at the start of the electrolytic metallization over the surface to be coated. The metal layer grows starting from the sites of electrical contact and spreads out over the entire surface.

A further method is described in EP 0 616 053 A1. According to this method a nonconducting substrate is initially treated with an activator comprising an inert metal sol with an additional metal from group IV A of the Periodic System of Elements (PSE). The activated surfaces are subsequently treated with a solution comprising a soluble metal salt, which is more inert than the metal of group IV A, and a metal hydroxide of group I A of the PSE, as well as a complex former with a complexation constant $\log K$ of approximately 0.73 to approximately 21.95 for the ions of the metal salt. The treated substrate can subsequently be electrolytically metallized.

For the generation of metal layers over the entire surface on the synthetic material layers, as a rule photoresist layers, required for the SBU technique, metal layers having uniform thickness cannot be generated using this method. To permit the adhesively strong coating of these surfaces, the layers must be considerably roughened. In the case of relatively large areas to be coated, metal layers are, consequently, generated at individual sites which have a relatively low thickness, while thicker metal layers are generated at other sites. While with minor roughening of the synthetic surfaces rather uniform metal layer thicknesses can be obtained, in this case, however, the adhesive strength of the metal layers on the synthetic surfaces is not sufficiently high.

The present invention therefore addresses the problem of circumventing the disadvantages of the known methods and to find, in particular, a method for the electrolytic deposition of a metal layer, in particular a copper layer, on surfaces of an electrically nonconducting substrate, in particular on larger electrically nonconducting surfaces, such as polymer surfaces. The method, for one, should also make possible satisfactory adhesive strength of the deposited metal layer on nonconducting surface areas and, for another, a uniformly thick metallization of large electrically nonconducting surfaces on circuit boards. In addition, the method is to be simple in execution and operable in a safe and problem-free fashion without expensive and complicated monitoring methods. The method is to ensure that the bath, unlike as in conventional electroless metallization baths, does not tend to self-decomposition.

The problem is solved through the method as claimed in claim 1 and the application of the method as claimed in claim 11. Preferred embodiments of the invention are specified in the dependent claims.

The invented method serves for the electrolytic deposition of a metal layer on surfaces of an electrically nonconducting substrate. In particular polymer surfaces, especially polymer resist layers, can be metallized using this method. Such polymer resist layers are utilized in more recent methods for the sequential structuring of multilayer circuit boards. For this purpose, circuit boards, optionally already provided with inner layers and on the outsides with circuit board patterns, are provided on one or both sides with a polymer layer, preferably a photoresist layer or a non-photosensitive lacquer or dry resist film. As photoresist layers are frequently employed commercially available photosensitive solder mask resist layers. However, different photoresists can also be utilized. Non-photosensitive polymer resist layers can be structured via laser ablation methods. In principle, a screen print lacquer can also be utilized. The lacquers or films are applied onto the circuit board outsides in conventional manner, for example by film transfer, curtain coating method, spin coating, roller coating, and the like.

For the subsequent production of electric interconnections between the individual wiring layers the polymer layer can be provided with holes. For this purpose photoresist layers with the

suitable pattern are exposed and subsequently developed, wherein the holes are formed. Such holes may have, for example, a diameter of approximately 100 µm and a depth of 70 to 120 µm.

On the polymer surfaces prepared thusly, a metal layer is applied according to the invented method. The formed metal layer is subsequently structured with the desired conductor track pattern, known structuring methods being used. The metal layer can be applied, for example, at a thickness corresponding to the conductor tracks to be formed and the regions of the metal layer not corresponding to the conductor tracks can subsequently be removed again using etching methods. Other methods for the formation of the conductor track pattern are well known in the field of technology.

After the conductor track patterns have been formed in this first conductor track plane, further planes can be produced in the same manner.

The method according to the invention for the generation of the first metal layer comprises the following method steps:

- (a) Activation of the surfaces with an inert metal colloid stabilized with compounds of a metal from the IVth main group of the Periodic System of Elements (PSE),
- (b) Treatment of the activated surfaces with an alkaline solution comprising ions of a metal more inert than the metal from the IVth main group of the PSE, and at least one complex former for the metal ions,
- (c) Bringing into contact the surfaces treated with the alkaline solution before the succeeding method step (d) is carried out, preferably within a time period of at most 60 seconds, with a copper bath comprising at least one copper ion source, at least one reducing agent for the copper ions, and at least one complex former for the copper ions, without application of an external current source,
- (d) Electrolytic deposition of the metal layer with a galvanization bath.

The copper bath utilized in method step (c) preferably does not comprise formaldehyde, but rather preferably compounds supplying hypophosphite ions as reducing agents.

The method according to the invention can be employed for the electrolytic metallization of polymer and copper surface regions on circuit boards. Such polymer surface regions are in particular the polymer layers applied on the outsides of the circuit boards during the application of the SBU method, as well as the resin surfaces in the bores exposed during the drilling in the conventional plating-through of circuit boards coated with copper foils. The method can advantageously be applied for coating polymer surface regions on the circuit boards, which originate from photoresist layers, for example of photosensitive solder masks, applied on the surface.

The method according to the invention entails the following advantages:

a. Due to the good electrical conductivity of the layer applied by the method steps (a) to (c),

relatively large nonconducting surface areas can also be electrolytically metallized without encountering problems. The problems known from electrolytic metallization, which can be traced back to the poor electrical conductivity of the known conducting layers, for example a palladium or tin sulfide layer, do not arise from the method according to the invention.

b. Large-area polymer layers, for example polymer layers which are applied over the entire surface on circuit boards and which do not include any metallic regions, can be coated with metal, such that the coatings have adhesive strength, and with a highly uniform layer thickness at all sites to be coated. It has been found that with the known methods, in particular with the direct galvanization method described in EP 0 616 053 A1 a uniform layer thickness of the metal layer cannot be achieved, if simultaneously the adhesive strength of the metal layer on the polymer layer is to be sufficiently high. To achieve sufficient adhesive strength, for example with a peel strength of at least 1 N/mm, measured in the peel test according to DIN, the polymer

layers must be roughened superficially with a suitable etching agent, for example in a permanganate etching process, wherein the roughness must not be too low.

It could be observed that the roughening of the surfaces of the polymer layers at different sites is also of different magnitude in particular if the roughening is overall relatively strong. The causes of these nonhomogeneities could so far not be elucidated. However, it is assumed that nonhomogeneous lamination and curing conditions for the polymer layers are the causes of these irregularities. After some investigations during the subsequent metallization with the known methods, it was further found that at such sites at which the roughness of the polymer surfaces is relatively high, a lesser thickness is achieved in the metal layer, while the metal layer thickness at surface regions with lesser roughness is greater. The reason is possibly that depressions in the rougher regions are filled first with metal and only then can the elevations be metallized, such that the metallization of these regions proceeds overall with greater difficulty. However, the mechanism which is, in fact, responsible for the differences in the layer thickness or whether there are several reasons for this occurrence, is not known.

With the newly found method these layer thickness differences can be evened out. By applying a further process step, in which the invented copper bath is utilized, at surface regions of different roughness layers of same thickness are also largely generated. The effect according to the invention occurs due to the surprising cooperation of the alkaline solution with the copper bath and immediately after the activated substrate surfaces are brought into contact. Therefore only very short treatment times are required such that in particular a treatment time with the copper bath of at most 60 seconds is sufficient. Preferably an even shorter treatment time with the copper bath is sought, for example at most 45 seconds and in particular at most 30 seconds.

c. The method suffices without complicated method steps. Thereby that preferably no copper deposition bath comprising formaldehyde is employed, the safety problems when using this volatile and toxic substance are not encountered. Further, the difficulties are not encountered which fundamentally occur with metal deposition baths containing formaldehyde, namely the tendency to spontaneous decomposition of these baths and the requirement resulting

therefrom of maintaining the bath parameters constant within narrow limits. For that reason the method with respect to the such parameters as concentration of the bath components, temperature and treatment time, can also be operated safely within wide ranges.

d. The entire method is extraordinarily short, as for each individual process step, i.e. also for the method steps (a), (b), and (d) only very short minimum treatment times must absolutely be maintained, which are in the range of a few seconds.

e. As significant roughening of the polymer layers is also possible without needing to anticipate considerable thickness differences of the metal layer on the surfaces to be coated, the roughening process as well as the further factors affecting the roughening, such as possibly the lamination and curing process for the polymer layer, do not need to be limited within narrow tolerance ranges.

f. Different metals can be applied onto the surfaces with the copper bath. In addition to a coating of electrically nonconducting surface regions, in the production of circuit boards most frequently individual copper regions must also be coated, for example in the metallization of holes in the polymer layer for the interconnection of several wiring planes, in which the conductor tracks of copper exposed at the bottom of the holes in the subjacent wiring plane must be coated. In this case there is frequently the requirement that no metals other than copper must be deposited in order not to run the risk that through intermediate layers of foreign metals inadequate adhesive strength results between two copper layers.

g. In the preferred embodiment in which in method step (c) a copper bath with compounds yielding hypophosphite ions are utilized as reducing agents, better values for the adhesive strength can be achieved than when using the conventional electroless copper deposition baths with formaldehyde as the reducing agent.

The metal bath according to the invention is preferably an aqueous solution comprised of copper ions from a soluble copper salt. Applicable are *inter alia* copper sulfate, copper chloride and copper acetate. The concentration of the copper ions is variable within wide limits. The

concentration may for example be in the range of approximately 0.01 M/L or even below that. The concentration can be increased up to the solubility limit. However, at higher concentrations there is the risk of spontaneous self-decomposition of the solution by precipitation of metallic copper. The concentration of the copper ions should therefore be in the range of approximately 0.01 mol/L to approximately 0.1 mol/L, preferably of approximately 0.01 mol/L to approximately 0.05 mol/L.

The copper bath preferably comprises in addition at least one nickel and/or cobalt ion source. Therewith the requisite treatment time in the copper bath is considerably shortened, for example to approximately 10 to 15 seconds. As nickel and cobalt ion sources, *inter alia*, nickel and cobalt salts may be utilized. The concentration of these salts is customarily in the range of approximately 0.0005 mol/L to approximately 0.01 mol/L, preferably of approximately 0.001 mol/L to approximately 0.005 mol/L.

The metal bath preferably comprises additionally at least one compound stabilizing the bath against decomposition, for example organic, in particular aromatic, sulfur compounds, in particular sulfur-containing compounds with nitrogen heterocycles, thiourea and its derivatives, metal cyanides and metal thiocyanates as well as metal selenocyanates, heavy metal compounds, such as mercury and lead compounds, or other stabilizing compounds, for example the compounds cited in DE 39 14 180 C2, US 3,607,317 A, US 3,615,737 A and US 4,301,196 A.

At least one of the parameters in the invented method, selected from the group consisting of the type of complex formers, the concentrations of the reducing agent, the nickel ion source, the cobalt ion source and the stabilizing compound in the copper bath as well as the pH value and the temperature of the copper bath, can further be so adjusted that the copper bath operates non-autocatalytically. Herewith further significant advantages of the method are attained.

Autocatalytic deposition of metal as understood here is characterized thereby that the metal is not only deposited on catalyzed surface regions, but also on surfaces of the same metal. In the present case according to the invention, in which the copper bath acts non-autocatalytically, copper is only deposited on the palladium nuclei formed in the activation,

which function as catalytic centers. However, as soon as in the advancing copper deposition the palladium nuclei have been completely covered by copper, the deposition virtually comes to a standstill.

A non-autocatalytic bath conforming to the invention is therefore *inter alia* present if the following is observed: a substrate with an electrically nonconducting surface, which has been pretreated according to the invented method according to method steps (a) and (b) and subsequently is brought into contact with the copper bath according to method step (c), is removed again from the bath after at least 20 minutes. During the subsequently bringing-into-contact-again no further metal deposition is detected in this case, wherein, however, it should be noted that the surface between the removal from the bath and the bringing-into-contact-again in the bath does not dry. In contrast, when using an autocatalytic copper bath, further copper is deposited after the surface is again brought into contact with the bath.

Furthermore, an autocatalytic copper deposition as understood here is characterized thereby that the copper is not only deposited on catalyzed surface regions, but rather also on pure copper surfaces. In this case copper is only deposited onto the palladium nuclei formed during the activation, which act as catalytic centers. However, as soon as with advancing copper deposition the palladium nuclei are completely covered by copper, the deposition virtually stands still. The copper from the invented bath is likewise also not deposited onto copper surfaces.

It has been found that copper baths are well suited for employment in the method according to the invention, if the baths have a satisfactory high stability according to the test stated in the following:

baths, which, in addition to the copper ions, comprise also a reducing agent, tend to decompose under metal deposition or precipitation of metallic copper in the deposition solution. To check the stability of a bath against this decomposition phenomenon, a test can be carried out, for example, in which the bath is heated to the temperature required for the application and subsequently, under effective and fast mixing, a defined volume of a solution comprising palladium ions or a palladium colloid solution is added. To check the stability, the time interval

is drawn on, which, starting with the addition of the palladium solution, has elapsed until the metal precipitates abruptly out of the solution. The longer this time interval, the more stable is the bath.

The above described method can also be drawn on for checking the suitability of the deposition bath in the method according to the invention. In the test applicable for this purpose, at the temperature required for the application, for example 50°C, is added to 250 mL of the solution to be tested, 1 mL of an aqueous palladium chloride solution (2.5 g Pd²⁺/L). It was found that the invented bath is especially suitable if no metal is spontaneously deposited out of the solution onto the container walls. If, in contrast, to an autocatalytically working bath a palladium ion-containing solution is added, gas development can already be observed after a short time and shortly thereafter also the formation of a copper mirror on the container wall. After carrying out this experiment, no more metal can be deposited from the bath decomposed in this manner, while a corresponding experiment with the bath according to the invention still proceeds successfully.

As complex formers for the copper ions in the copper bath are preferably employed carboxylic acids and their salts. Complex formers are preferably utilized which are biologically readily degradable. Among them are in particular tartaric acid and citric acid as well as their salts. Applicable are also lactic acid, maleic acid and succinic acid. The concentration of these substances should be high enough for the ions contained in the copper bath to be completely complexed. This means that in most cases as the lower limit a molar ratio of the quantity of complex formers to the quantity of copper of 1 to 1 is to be set. Depending on the stoichiometry, in many cases a ratio of 2 : 1 may also be necessary. An upper limit results only from the demand that the complex former must be soluble in the bath. If, for example, a copper bath with a copper content of approximately 0.015 mol/L is used, the content of trisodium citrate can be approximately 0.1 mol/L. As the compounds supplying hypophosphite ions the copper bath comprises further preferably a hypophosphite salt, such as sodium hypophosphite, or hypophosphoric acid. The concentration of these substances is preferably in the range of approximately 0.2 mol/L to approximately 1 mol/L.

The pH value of the copper bath is preferably adjusted to approximately 9 to approximately 13, in particular to approximately 10 to approximately 12. For the adjustment are used acids, for example boric acid and/or hypophosphoric acid, or bases, for example sodium hydroxide and/or trisodium citrate.

Treatment with the copper bath can be carried out at a temperature of approximately 25 to approximately 95 °C. A favorable temperature range was found to be approximately 35 to approximately 70 °C and in particular approximately 40 to approximately 50 °C. Higher temperatures lead more readily to the spontaneous self-decomposition of the bath, they have, however, the advantage that a visible copper layer is formed within a shorter time. In the presence of lower layer thicknesses only a reddish discoloration of the substrate can be observed, while a thicker layer is indicated by a metallic luster.

The copper deposition with the copper bath is initiated entirely without application of an external current source, in that the substrate surfaces are previously catalyzed with the activator according to method step (a) and the alkaline solution according to method step (b).

If circuit boards are treated with the invented method in a so-called horizontal installation, in which the boards are preferably transported in the horizontal direction from one treatment module for a method step to the next, very short treatment times can be reproducibly maintained. Under these conditions, the circuit boards are brought into contact with the copper bath for a treatment time of approximately 15 to approximately 60 seconds, preferably from approximately 30 to approximately 45 seconds.

In method step (a) the substrate is activated with an inert metal colloid. As colloid is preferably utilized a palladium/tin colloid. Such colloids are known *per se*. The palladium colloid in this case is stabilized by tin(II)/tin(IV) oxychlorides. Such colloids are produced through the reduction of palladium chloride in hydrochloric acid solution with tin(II) chloride. The production method for such palladium colloid solutions stabilized with tin compounds are described for example in DE-A 29 28 699, EP-A 0 109 402, US-A 3,532,518, EP-A 0 191 433

and US-A 3,874,882. When applying the horizontal technique, the treatment time in the inert metal colloid is approximately 45 to approximately 60 seconds.

After the activation the substrate is treated in method step (b) with an alkaline solution. This solution is preferably an aqueous alkaline solution, which, in addition to the metal ions, preferably copper ions, comprises at least one complex former for the metal ions. For the formation of the metal ions the solution may contain conventional metal salts, preferably copper salts. As complex formers can be used for example a hydroxycarboxylic acid, such as tartaric acid, citric acid or their derivatives. The concentration of the metal ions is in the range of approximately 0.0002 mol/L to approximately 0.2 mol/L, preferably in the range of approximately 0.004 mol/L to approximately 0.01 mol/L, the concentration of the complex formers in the range of approximately 0.05 mol/L to approximately 1.0 mol/L and in particular in the range from approximately 0.2 mol/L to approximately 0.5 mol/L.

The alkaline solution further comprises a metal hydroxide or another aqueous alkaline hydroylizing compound in water, for example sodium hydroxide and/or trisodium citrate. The solution should preferably be adjusted to a pH value of at least approximately 11, preferably in the range of approximately 11.5 to approximately 13. The treatment time in the alkaline solution when applying the horizontal technique, is approximately 45 to approximately 60 seconds.

Following the treatment with the alkaline solution, the substrate surfaces are treated with the copper bath according to the invention. The electrolytic metal layer can subsequently be formed with a commercially available galvanization bath. A galvanic copper bath, for example a sulfuric acid copper bath, is conventionally utilized for the deposition of a copper layer. It is understood that other metals can also be deposited electrolytically, for example nickel, gold, tin, lead and alloys of these metals.

In addition to the method steps described above, further method steps can be applied for optimization of the process result, in particular for the production of circuit boards:

- (i) pretreating the polymer surfaces, for example of a photosensitive solder mask

layer, with conventional etching methods, for example with a permanganate treatment (swelling in an organic solvent, etching in, for example, a 80°C hot alkaline permanganate solution, removing of manganese dioxide formed during the etching); alternatively, other synthetic material etching methods can also be applied, for example a method based on chromic acid or chromic/sulfuric acid;

- (ii) optionally cleaning the exposed synthetic material surfaces, for example with alkaline solutions comprising wetting agents, triethanol amine and other cleaning agents;
- (iii) before the treatment with the inert metal colloid according to method steps (a): conditioning of the surfaces with a conditioning bath comprising at least one substance for promoting the adsorption of inert metal nuclei, preferably of metallic palladium nuclei, on the nonconducting surfaces containing conditioning bath, for example with an alkaline or acidic solution of cationic polyelectrolyte compounds, polymeric amines and/or quaternized ammonium compounds; quaternized polyvinyl imidazole can preferably be utilized;
- (iv) after the treatment with the conditioning bath and before the treatment with the inert metal colloid according to method step (a):
 - initial etching of exposed copper surface regions with an etching cleaning bath comprising at least one compound with an acidic reaction in water and at least one oxidizing agent for copper; in the etching cleaning bath are preferably comprised as the oxidizing agent sodium peroxodisulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and a compound with an acidic reaction selected from the group comprised of acidic sulfate salts, methanosulfonic acid and sulfuric acid;
- (v) pretreating of the surfaces with a solution comprising a portion of the substance also contained in the inert metal colloid solution (pre-dipping solution).

For the alternative case, in which the method according to the invention is utilized for the through-plating of circuit boards, the above method steps are also carried out.

The above method stages are conventionally worked through in the stated sequence.

However, in principle, the etching cleaner can also be applied before the conditioning of the surfaces. Depending on the application case, it is also conceivable to carry out the method without one or several of the method stages (i) to (v) or without all of these method stages.

Except between stages (v) and (a), between each of the method stages (a) to (d) and (i) to (v) a rinsing process is carried out.

To improve the quality of the deposited copper layers and to increase the adhesive strength of the metal layers on the substrate surfaces, the substrates can be tempered after completion of the permanganate treatment and/or after the electrolytic deposition of the metal layer, preferably after formation of the entire metal layers, in order not to have to interrupt the galvanic process additionally. For this purpose the substrates are heated, for example, for two hours at approximately 180°C.

The invented method can be utilized for the production of circuit boards. The circuit boards can, for example, be dipped sequentially into the individual baths and be treated therein for the specified treatment times. However, a technique referred to as horizontal technique, is preferably utilized, in which the circuit boards, disposed in the horizontal or in the vertical position, are fed through a treatment installation on a horizontal transport path. During the transport through the installation the individual treatment solutions are sprayed, squirted or splashed against the circuit board from below and/or above the transport path.

In the following, examples of the method according to the invention are provided:

Example 1

A circuit board (so-called multilayer) with bore holes and inner copper layers was treated in a conventional permanganate method with an organic sweller, alkaline permanganate etching solution and acidic hydroxylamine solution for the bore hole cleaning.

The circuit boards were subsequently further treated as follows by dipping them into the particular treatment solutions:

	Conditioning with an aqueous solution comprising an alkaline quaternized polyamine, for example conditioner NEOPACT® UX (Atotech Deutschland GmbH)	°C	60	12
	Rinsing		0 sec	
		R	60	
		T	sec	
	Etching cleaning of the copper surfaces with an aqueous solution (30 g/L Na ₂ S ₂ O ₈ / 30 g/L NaHSO ₄)	R	12	
	Rinsing	T	0 sec	
		R	60	
		T	sec	
	Predipping with 10 wt% HCl	R	60	
		T	sec	
	Activating with commercially available palladium/tin activator	°C	40	18
	Rinsing	0 sec		
		R	60	
		T	sec	
	Treating with the alkaline solution	°C	60	60
		sec		

	Treating with the copper bath Rinsing	$^{\circ}\text{C}$	50 sec	90 sec
		R		60
		T	sec	
	Electrolytic copperplating in a commercially available sulfuric acid-containing copper bath, for example CUPRACID® BL (Atotech Deutschland GmbH), Current density: 2 A/dm ²		0 sec	12

RT: Ambient temperature (20 to 25 °C)

The activator (inert metal colloid) was produced by mixing 300 mL 37 wt.% HCl, palladium chloride in a quantity corresponding to 250 mg Pd, and 17 g SnCl₂ in water to yield 1 L solution.

The alkaline solution was produced by mixing 25 g LiOH, 20 g NaOH, 4 g CuSO₄ · 5 H₂O and 15 g tartaric acid in water to yield 1 L solution. The pH value of the solution was adjusted to 13.

The copper bath comprised the following components, which were dissolved in water:

CuSO₄ · 5H₂O 6.0 g

CoSO₄ · 7H₂O 0.4 g

Trisodium citrate · 5.5H₂O 32 g

NaH₂PO₂ · H₂O 50 g

Boric acid 35 g

NaCN 3 g

Dissolved in 1 L of water

pH value adjusted with NaOH to ≈ 12

Temperature 30 to 45 (40) °C

After briefly dipping the circuit boards treated with the alkaline solution, a color shift of the grey fogging, generated by the treatment with the activator, toward a reddish tint could already be observed. This indicates a fast reaction of the copper bath with the treated surface.

In the subsequent electrolytic metallization a completely closed copper layer was obtained on the circuit board. To test that the electrolytic copper layer was also formed continuously without a gap on the bore hole walls, the circuit board was cut along a row of holes and at a small distance from this cut a second cut was made parallel to it, such that light irradiated from the second cut into the circuit board material could leave the hole walls substantially perpendicularly if the layer at that site was not closed. With the aid of a microscope therewith extremely small fault sites in the metallization could be detected as points of light (transmitted-light test).

In a second test the circuit board treated according to the example and copperplated to a thickness of 25 μm was dipped successively first for 10 sec into a 288°C hot solder bath and subsequently cooled in air to ambient temperature. After carrying out the solder shock, a transverse section of the copperplated bore was produced. However, possible tearing of the metal sleeve in the bore from the front sides of the inner copper layers was not observed in the transverse section.

Example 2

Example 1 was repeated with the following copper bath solution:

<chem>CuSO4</chem> · 5H ₂ O	9.0 g
<chem>NiSO4</chem> · 6H ₂ O	0.5 g
Potassium-sodium tartrate · 4H ₂ O	30 g
<chem>NaH2PO2</chem> · H ₂ O	40 g
Boric acid	20 g
Pb ²⁺ (as Pb(OAc) ₂)	20 mg
Dissolved in 1 L of water	
pH value adjusted with NaOH to	≈ 12
Temperature	50 °C

Again, a slight color shift of the gray fogging on the bore hole walls, generated through the treatment with the activator, toward a reddish tint could be observed. During the subsequent metallization a completely closed copper layer with high adhesive strength on the base was formed.

Example 3

Example 1 was repeated with a circuit board material which did not have any copper lamination on the outside, but rather was provided with an approximately 70 µm thick layer of a photosensitive solder resist mask. In the solder resist mask layer by exposure with a suitable pattern and subsequent development of the layer, extremely fine holes with a diameter of 100 µm were introduced. The holes completely penetrated the resist layer, such that subjacent conductor tracks of copper were exposed at those sites at which the holes were located.

After carrying out the permanganate method, the material was tempered for two hours at 180°C. The method sequence of Example 1 was subsequently repeated and after the deposition of 35 µm copper over the entire surface, was again tempered in the same manner.

A complete coverage of the circuit board with copper including the coating of the holes was obtained. The peel strength of the copper on the surface according to the DIN peel test was determined with a tensile test device. An adhesive strength of approximately 1.8 N/mm was attained.

The electrical conductivity of the treated polymer resist surfaces was determined after different process steps and different treatment times with a simple two-point method, in which two metal tips were pressed onto the resist surface at a distance of 1 cm from one another.

After the treatment of the resist layer in the alkaline solution, a resistance of 120 kOhm was measured. In the subsequent treatment in the copper bath, after a very short time already a rapid drop of the resistance (rise of conductivity) was observed: after a treatment time of 10 seconds, the resistance was 230 Ohm, after 20 seconds 33 Ohm and after 40 seconds 6 Ohm.

Example 4

Example 1 was repeated. However, the circuit board was treated in a horizontal installation, in which the circuit board material was transported in horizontal orientation. The individual treatment solutions were delivered to the circuit board surfaces with splash nozzles. The circuit boards, which were lined up with cylinders disposed at the entrance into the treatment modules and at the exit from the individual treatment modules, were conducted through the individual solutions. To the extent the method steps were also carried out in Example 1, the treatment solutions utilized were identical.

The treatment conditions (temperature, treatment time) are given in the following:

	Sweller Securiganth® SBU (Atotech Deutschland GmbH); aqueous solution of organic solvent)	°C	90	12
	Rinsing	T	0 sec	
		R	10 sec	
	Permanganate solution (70 g/L MnO ₄ ⁻ , 50 g/L NaOH)	°C	80	24
	Rinsing	T	0 sec	
		R	10 sec	
	Reducing solution Securiganth® P500 (aqueous solution of hydroxyl ammonium chloride)	°C	45	60
	Rinsing	T	sec	
		R	10 sec	
	Conditioner	°C	50	15
	Rinsing	T	sec	
		R	10 sec	

	Etching cleaner	C	30	15
	Rinsing	R		sec
		T	10	sec
	Predipping	R	15	
		T		sec
	Activator	°C	32	55
	Rinsing	R	10	
		T		sec
	Alkaline bath	°C	47	55
	Rinsing	R	10	
		T		sec
	Copper bath	[°C]	50	40
	Rinsing	R	10	
		T		sec
	Electrolytic copperplating			12
				0 sec

The same results as in Example 1 were again attained.

Patent Claims

1. Method for the electrolytic deposition of a metal layer on surfaces of an electrically nonconducting substrate, in particular on polymer surfaces, with the following method steps:

- (a) Activating the surfaces with a noble metal colloid, which is stabilized with compounds of a metal from main group IV of the Periodic System of Elements,
- (b) Treating the activated surfaces with an alkaline solution comprising ions of a metal more inert than the metal of main group IV of the Periodic System of Elements, and at least one complex former for the metal ions,
- (d) Electrolytically depositing the metal layer with a galvanization bath,

characterized in that

(c) the surfaces treated with the alkaline solution before carrying out method step (d) are brought into contact with a copper bath comprising at least one copper ion source, at least one reducing agent for the copper ions and at least one complex former for the copper ions, without application of an external current source.

2. Method as claimed in claim 1, characterized in that the surfaces of the electrically nonconducting substrate are brought into contact with the copper bath for at most 60 seconds.

3. Method as claimed in one of the preceding claims, characterized in that as the reducing agent in the copper bath compounds supplying hypophosphite ions are utilized.

4. Method as claimed in one of the preceding claims, characterized in that the copper bath comprises additionally at least one nickel and/or cobalt ion source.

5. Method as claimed in one of the preceding claims, characterized in that the copper bath additionally comprises at least one compound stabilizing the bath against decomposition.

6. Method as claimed in one of the preceding claims, characterized in that at least one of the parameters, selected from the group comprising the type of the complex former, the concentrations of the reducing agent, the nickel ion source, the cobalt ion source and the stabilizing compound in the copper bath as well as comprising the pH value and the temperature of the copper bath, is adjusted such that the copper bath operates non-autocatalytically.

7. Method as claimed in one of the preceding claims, characterized in that as complex former for the copper ions are utilized carboxylic acids and their salts.

8. Method as claimed in one of the preceding claims, characterized in that as the inert metal colloid in method step (a) a palladium/tin colloid is utilized.

9. Method as claimed in one of the preceding claims, characterized in that as metal ions in the alkaline solution in method step (b) copper ions are utilized.

10. Method as claimed in one of the preceding claims, characterized in that, before the treatment with the inert metal colloid according to method step (a), the surfaces are treated with a conditioning bath comprising at least one substance for the promotion of adsorption of inert metal nuclei on the nonconducting surfaces.

11. Application of the method as claimed in one of claims 1 to 10 for the electrolytic metallization of polymer and copper surface regions on circuit boards.

12. Application as claimed in claim 11, characterized in that the polymer surface regions on the circuit boards are formed of polymer resist layers.